

*The Thermal Effects produced by Heating and Cooling
Palladium in Hydrogen.*

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It is agreed by all observers that a change in the extent to which hydrogen is occluded by palladium takes place at a temperature of about 100° C. This change might be the result of (1) a polymorphic transformation in the metal, or of its surface layer; (2) the formation or dissociation of a compound or solid solution with hydrogen, and, further, the occlusion may be of a dual nature—surface adsorption and diffusion into the metal—these phenomena may take place at different temperatures.

Since the pressure-temperature-concentration relations of hydrogen to palladium have already been the subject of detailed investigations by Hoitsema (1), Roozeboom, and others, and the changes in electrical resistance resulting from occlusion of the gas have been examined by Fischer and Sieverts (2), it appeared advisable to attack the problem from a thermal standpoint, since it has been found that occlusion of hydrogen by the metal is accompanied by an evolution of heat.

This aspect of the question has already been the subject of experiments by Ramsay, Mond, and Shields (3), who argue that if the heat evolution is solely the result of condensation of the gas, the heat evolved during the condensation of equal volumes of hydrogen by different metals should be the same. Calorimetric observations by these authors showed that this was not the case, at any rate for palladium and platinum, the values obtained exhibiting a greater divergence than could be accounted for by experimental error.

The above hypothesis assumes that the gas is condensed in a similar manner by the two metals, but the great difference in the volumes occluded by unit volume of each metal does not, however, support this contention. For example, suppose the gas to be merely condensed on the surface of the one metal either as molecules, or molecular complexes, whilst in the other case it is dissolved in the atomic condition. In both cases a certain amount of heat would be evolved, but in the latter this amount would be diminished by that absorbed in dissociating the gas molecules into atoms, the heat of solution of the gas in this condition not being taken into account.

Little is known concerning the condition of the hydrogen occluded by palladium. From density determinations it appears that the gas is present in a quasi-solid condition, whilst the experiments of Sieverts (2), point to the probability that at temperatures up to the melting point of the metal the gas is dissolved in the atomic state.

Holt, Edgar, and Firth (4) have shown that a close analogy exists between the phenomena of occlusion of hydrogen by palladium, and by charcoal, and according to McBain the gas absorbed by charcoal is present as atoms.

Since any change in the condition of the gas must be accompanied by an evolution or absorption of heat, the study of heating and cooling curves of hydrogen-palladium should afford valuable data, and it is the study of such curves that constitutes the present communication.

Palladium in three different forms was used for the experiments: thin foil (about 0.1 mm. thick), black, prepared by strongly igniting palladium ammonium chloride, and fused metal in the form of a button. The metal was heated in either hydrogen, air, or *in vacuo*, in an electrically heated porcelain tube furnace. The whole apparatus is illustrated in fig. 1. The

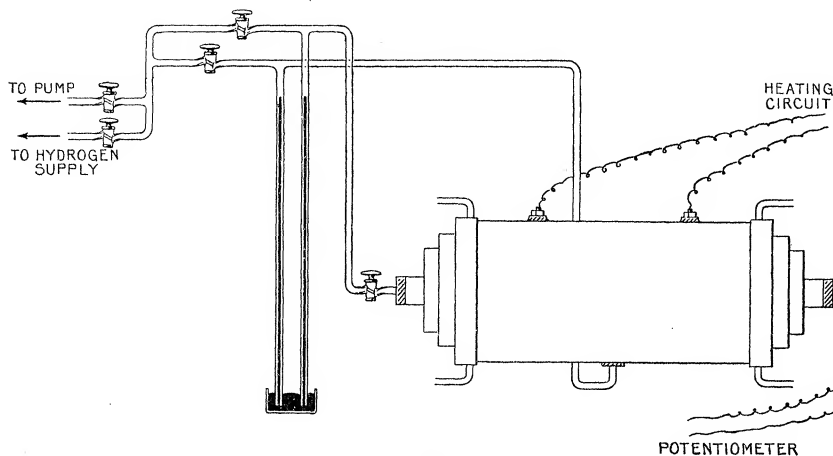


FIG. 1.

furnace was so constructed that a vacuum could be maintained on the outside of the heated portion of the tube, in order to give a uniform rate of cooling. The outer jacket consisted of a hard drawn copper tube, to which gunmetal ends were brazed. Between these ends and the porcelain tube were inserted rubber rings, which could be expanded by means of screw caps, thus forming air-tight connections between the tube and outer jacket. The porcelain tube was surrounded by water coolers at both ends. The leads for the heating circuit were passed through air-tight insulators in the outer jacket. Upon

evacuating the space between the tube and outer jacket, it was found possible, on account of the vacuum and high reflecting power of the copper, to cool the furnace at a regular and comparatively rapid rate, even at low temperatures. Full details of the furnace are to be found in a previous publication of one of the authors (5).

For detection of thermal changes in the palladium, a platinum-platinum-iridium thermocouple, previously calibrated over the range of temperature concerned, was employed.

In the case of the fused button of palladium, contact was made by inserting the thermocouple into a small hole drilled in the specimen, whilst when using palladium foil or black, the metal was enclosed in a quartz tube and closely packed round the end of the couple, a pad of asbestos keeping the whole in position.

The wires from the thermocouple lying inside the furnace were insulated from each other by means of a two-hole fireclay tube, and passed through a rubber stopper, which made an air-tight joint at one end of the porcelain tube. Outside the stopper they were soldered to copper leads, which in turn were connected through a Carpenter-Stansfield potentiometer to a d'Arsonval mirror galvanometer. The cold junctions were kept at 0° C. by immersing in ice.

The other end of the porcelain tube was connected to a manometer, hydrogen reservoir, and an automatic sprengel pump with three fall tubes, the details of this portion of the apparatus being apparent from the illustration.

The experiments grouped themselves into five categories:—

- (i) Heating and cooling the metal *in vacuo*.
- (ii) Heating and cooling the metal in hydrogen, after allowing it to occlude gas in the cold, until the initial heat evolution had ceased, and the metal had regained its normal temperature.
- (iii) Heating and cooling the metal in hydrogen immediately after the above treatment, and consequently without preliminary occlusion of gas and evolution of heat.
- (iv) After cooling in hydrogen and evacuating in the cold, the metal was heated, and the gas still occluded was continuously removed by the pump.
- (v) Admitting hydrogen to the metal heated *in vacuo*, and cooling in the gas.

In all experiments the hydrogen was maintained at a constant pressure, slightly higher than that of the atmosphere, in order to prevent inward diffusion of air through the rubber stoppers.

The first series of experiments in which heating and cooling curves of the metal *in vacuo* were taken are illustrated in figs. 2 and 3. In the actual experiments, time readings were taken at constant intervals of temperature, and the differences in time taken to cool, or heat up, through this constant

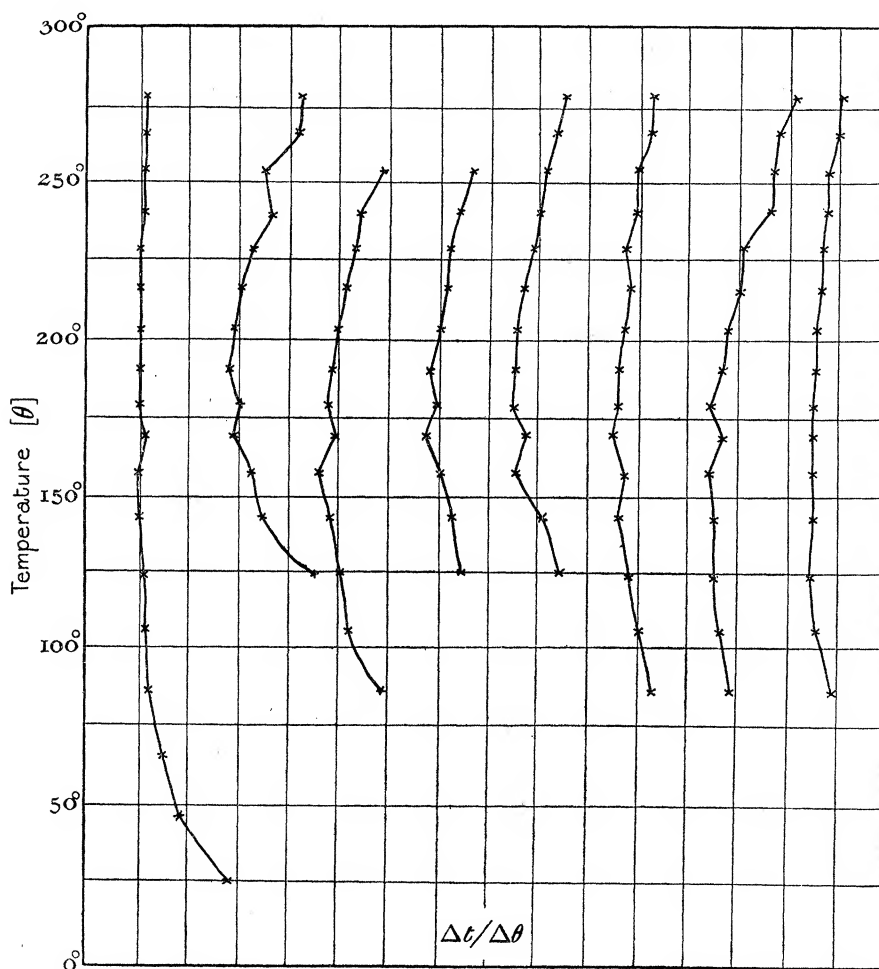


FIG. 2.—Heating Curves of Palladium *in vacuo*.
Nos. 1-7. Palladium foil. No. 8. Palladium black.

temperature interval, at different temperatures, are plotted against actual temperature readings.

The method of plotting is what is generally known as the "inverse rate method," the values of $\Delta t/\Delta \theta$ being plotted against those of θ , where t = time and θ the temperature.

It will be seen from figs. 2 and 3 that, whilst no thermal effect of any

magnitude is indicated, small changes in the slope of the curve are apparent at certain temperatures. These might be attributed to experimental error, since they are of very small order, were it not for the fact that the temperature ranges over which they persist are nearly coincident in all the

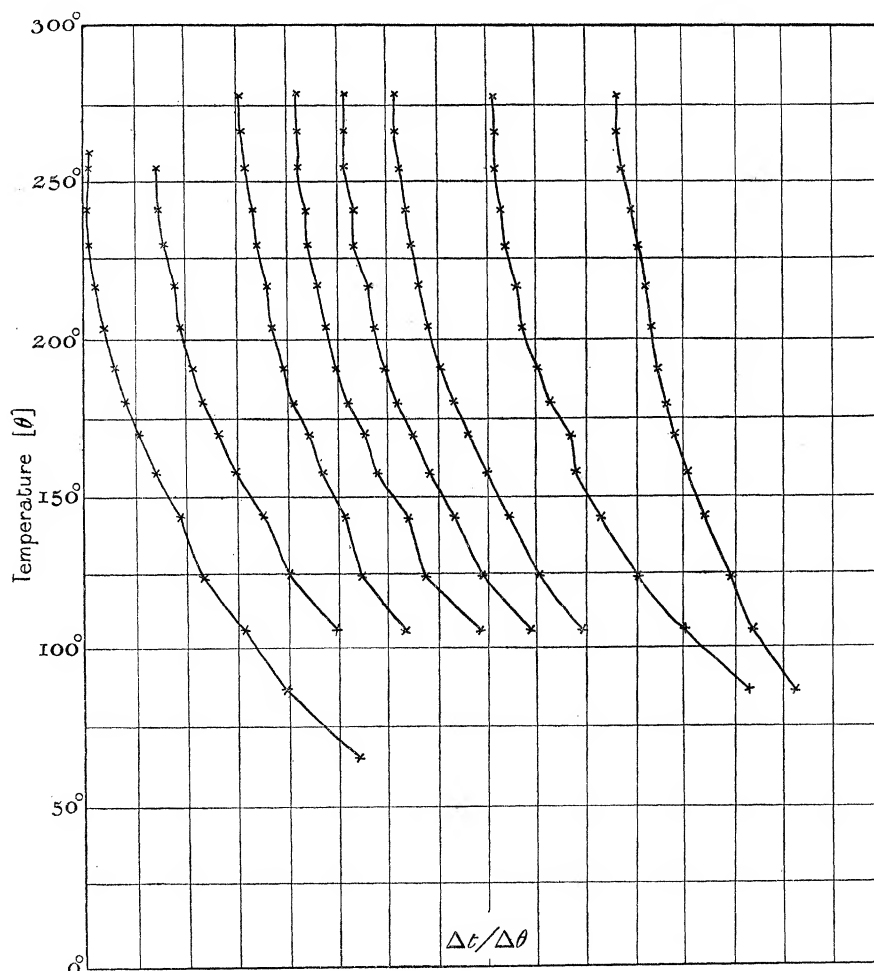


FIG. 3.—Cooling Curves of Palladium *in vacuo*.
Nos. 1-7. Palladium foil. No. 8. Palladium black.

curves. More probably they are an indication of some transformation within the metal, since they represent heat absorption during heating and heat evolution on cooling—complementary effects. If a slow change over a wide range of temperature took place, no great deviation from normal heating and cooling curves would be apparent.

Though the results of the above curves are by no means conclusive, the

authors are inclined to believe that they do indicate an allotropic change, and this belief is strengthened by a consideration of the experimental work of other investigators on hydrogen-palladium.

Palladium black, even after an interval of many years, appears always to possess the property of immediately occluding hydrogen, with evolution of heat. A sample of black which had been untouched for over 30 years was found to be in no way different from the freshly prepared substance. If, however, a sample of black be melted into a metallic bead, this property is almost entirely destroyed. Such an inactive bead can, however, always be reactivated by heating to a red heat in air. The probable effect of this treatment is to produce a film of oxide, which in the presence of hydrogen is at once reduced, giving a surface of spongy metal intensely active towards hydrogen. On long standing this property dies away, a phenomenon not observed in the case of palladium black. The reduction of an oxide by hydrogen, or the decomposition by heat of such a compound as ammonium palladium chloride, gives rise to the production of amorphous palladium, which, if uncontaminated by the stable crystalline form, undergoes no change. This would satisfactorily explain the activity of palladium, for whilst the pure amorphous black (which alone appears to possess the property of rapid occlusion of gas) would remain in the meta-stable condition, a film of spongy amorphous metal on a crystalline mass would gradually tend to crystallise, owing to the presence of the stable phase.

A somewhat parallel case is that of grey and white tin. Each variety apart from the other is more or less stable, but if present together in physical contact (as in the case of a mass exhibiting both varieties) the meta-stable passes gradually to the stable form.

It is stated by Ramsay, Mond, and Shields that a unit mass of palladium in any form will occlude the same volume of hydrogen. This occlusion may be, and probably is, an intrinsic property of the metal, but the extreme variation in the rate of initial occlusion of gas, as well as the decay of this rate with time, requires a separate explanation, and the above hypothesis appears to satisfy the experimental observations.

It has been pointed out that palladium black is probably amorphous, since it has been produced by decomposing a compound at a temperature lower than that at which the metal melts, and crystallisation in the case of a metal is usually associated with cooling from the liquid state, and it is this form alone which is able to bring about rapid occlusion of the gas.

It is now usually believed from the work of Beilby(6), Bengough(7), Rosenhain(8), and others, that under certain conditions the crystals of a metal are surrounded by an amorphous metallic cement. Beilby showed

that this amorphous material is readily formed upon subjecting the metal to strain, the slipping of the crystals over one another giving rise to its formation. Bengough, however, considers that this amorphous material is present in all metals and alloys, whether they have undergone any mechanical treatment or not. Both, however, consider that this cement ultimately disappears with rise in temperature, the temperature at which it ceases to exist differing in each metal. Rosenhain has carried the matter further still, and quotes experiments to prove the existence of this amorphous cement at all temperatures below the melting point.

If this be the case, it follows from what has been said that palladium cooled from the molten state will contain a minute amount of amorphous matter, and hence should exhibit the power of rapid occlusion of the gas very feebly.

It was found that the activity of palladium in the massive state was considerably affected by first allowing it to occlude gas and then pumping it off; not only was its activity preserved, but it was increased. In the May lecture of the Institute of Metals, 1911, Dr. Beilby makes the following suggestion with regard to the action of gases upon crystallisation. He says: "The gas molecules as they find their way among the metal molecules of the solid are quite capable of producing sufficient movement to arrest crystallisation, or even to flow the crystals which are already formed into the amorphous variety." Dr. Beilby's theory offers a very likely explanation of this increased activity, the continual occlusion and extraction of the gas giving rise to the production of the active amorphous phase.

This view would certainly explain the great changes in the rapidity of the initial occlusion with alteration in the state of the metal. The gas no doubt does subsequently diffuse right into the crystals of the metal, but extremely slowly. A microscopical examination of the surfaces of the palladium before and after saturation with hydrogen exhibited no striking features. In each case the metal was found to be highly crystalline. The surface of the specimen which had been previously saturated with hydrogen had a distinctly pitted structure, dark blotches distributed in an irregular manner throughout the metal being evident. It is quite probable that these dark markings are due to the presence of the amorphous metal formed during the evolution of hydrogen. Palladium black appeared as amorphous grains, with no trace of crystalline structure.

The second series of experiments (in which the metal, after the preliminary heat evolution due to initial occlusion of gas had ceased, was heated and cooled in hydrogen) will next be considered. As has already been mentioned, palladium, in any form except black, will sometimes pick up gas with avidity,

and at others with extreme slowness, the heat evolution varying in a parallel manner with the rate of occlusion.

Some measurements of this heat effect have been made, which although by no means accurate, on account of the unsuitability of pyrometric measurements for such determinations, are of interest as showing the great differences which occur. Some values are given in the subjoined table.

Condition of metal.	Temperature before admission of gas.	Rise in temperature after admitting gas.
	° C.	° C.
Black	15	60
Black	310	5
Fused mass.....	15	3
Fused mass.....	310	7
Foil (0.1 mm. thick)	310	3

From these figures, it is evident that, when hot, the heat evolution is practically a constant, no matter what the condition of the metal may be, whereas at the ordinary temperature of the laboratory (about 15° C.) the condition of the metal makes an enormous difference. Hence it may be concluded that when hot the amount of gas picked up by unit mass of metal is constant, and characteristic of the metal, whilst when cold some other influence comes into play. It should be remarked that whilst the heat evolution in the case of the black remains fairly constant (at about 15° C.), with the fused mass it varies somewhat according to the state of its surface.

Determinations were also made to ascertain the heating effect produced by admitting hydrogen to palladium black, at intermediate temperatures between the limits cited. The results are as follows :—

Initial temperature at which hydrogen was admitted.	Rise in temperature.
° C.	° C.
15	53
103	21
120	15
253	8

The rise in temperature, therefore, decreases with the absolute temperature of the metal, as is to be expected from the temperature-concentration relations. The initial heat evolution upon admission of hydrogen is followed by an extremely rapid cooling, more rapid indeed than could be expected from normal cooling, indicating the probability of an endothermic change.

After hydrogen had been admitted to the metal, in the cold, and after any initial thermal effect had died away, the metal was then heated in the gas and heating curves taken. Such curves are shown in fig. 4.

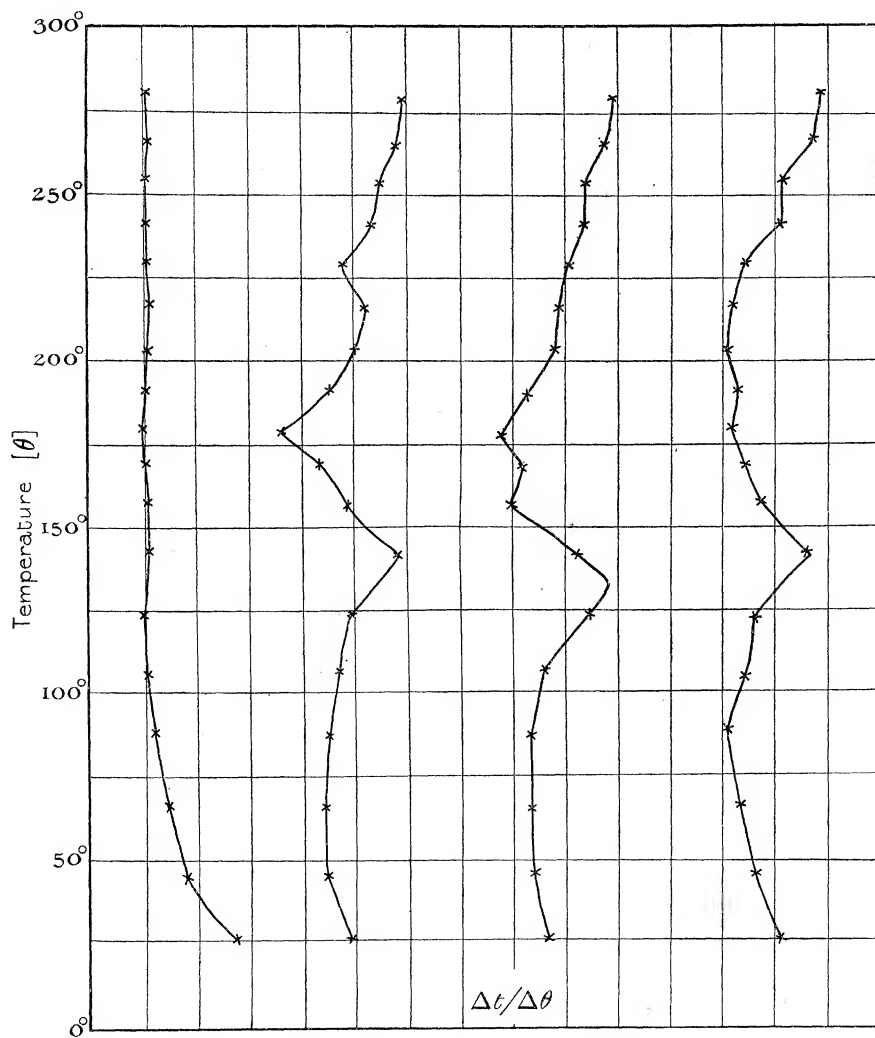


FIG. 4.—Heating Curves of Palladium in Hydrogen.

- No. 1. Palladium foil which had evolved no heat upon admitting hydrogen at 15° C.
- No. 2. Palladium foil which had evolved heat and occluded hydrogen at 15° C.
- No. 3. Palladium black which had evolved heat and occluded hydrogen at 15° C.
- No. 4. Palladium button which had evolved heat and occluded hydrogen at 15° C.

These curves can be divided into two classes, according as they do, or do not, exhibit any critical points, and it is remarkable that such points are only shown when there has been initial heat evolution upon admitting gas in the

cold. The critical points, whether for black, foil or fused button, all possess a similar character.

An absorption of heat begins at about 95° C., and continues up to a temperature of about 135° C., at which temperature a rapid evolution of heat begins. The absorption of heat between 95° and 135° C. corresponds exactly with the range of temperature over which the great decrease in solubility of the gas in the metal occurs, for at 95° C. (according to Hoitsema's values) about 750 volumes of gas at atmospheric pressure are retained by one volume of the metal, whereas at 135° C. the solubility has decreased to about 100 volumes.

When it is considered that critical changes are only observed when a heat evolution has followed the admission of hydrogen in the cold, and as condensation would cause such a thermal change, an absorption of heat over a temperature range during which most of the occluded gas is being evolved is a natural consequence.

In fig. 5 are shown the cooling curves obtained when the metal after heating in hydrogen was allowed to cool in the gas.

On cooling no prominent points were observed unless the metal had rapidly absorbed gas in the cold and given it off between 95° and 135° C. on heating.

On cooling a heat evolution commences at about 135° and ceases about 105° C., this latter temperature varying somewhat with the condition of the metal. Thus, for palladium black, the heat evolution ceases about 120° C., whilst for palladium foil it ceases about 100° C. It is evident that whatever may be the nature of occlusion, the process is reversible, the evolution of heat on cooling, and absorption of heat on heating, taking place practically over the same temperature, the former heat effect being due to occlusion of gas, and the latter to its evolution. After the metal had completely cooled in hydrogen, it was reheated in the gas. The heating curves are shown in fig. 6.

As might be expected, they are very similar in character to those of fig. 4, but it is remarkable that the temperature of the critical points in the case of palladium foil and fused button varies greatly according to the time the metal has remained in contact with the gas in the cold.

If the re-heating took place almost immediately after the metal had cooled, the point coincided with a temperature of about 140° C., whilst if it had remained a week after cooling the point was raised to about 235° C., and intermediate temperatures were observed for shorter periods of time at room temperature.

In the case of palladium black, this effect was not observed. It would

seem, therefore, that when the ratio of surface to mass of metal is not too great, a time limit affects the temperature at which the gas is given off on a somewhat rapid heating, for the point again coincides with rapid evolution

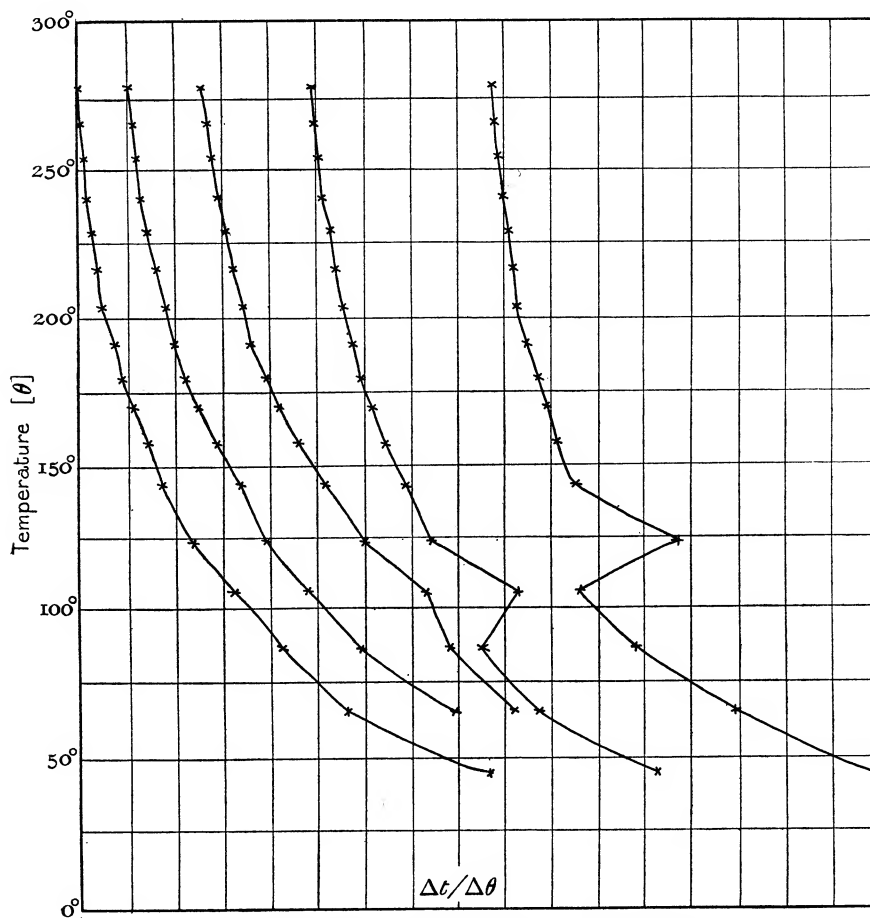


FIG. 5.—Cooling Curves of Palladium in Hydrogen.

- No. 1. Palladium button only slightly active towards hydrogen.
- No. 2. Palladium foil only slightly active towards hydrogen.
- No. 3. Palladium foil more active towards hydrogen than in the case of No. 2.
- No. 4. Palladium foil very active towards hydrogen.
- No. 5. Palladium black very active towards hydrogen.

Note.—When the palladium button became active, a series of curves similar to Nos. 2, 3, and 4 were obtained.

of the gas. With very slow heating this difference in temperature is found to be less apparent, so that the effect may be due to a difficulty experienced by the gas in rapidly escaping, otherwise it must be concluded that the

pressure-concentration values vary with the length of time the metal has remained in contact with hydrogen.

A comparison of these curves with those of fig. 4 shows that, in the case of

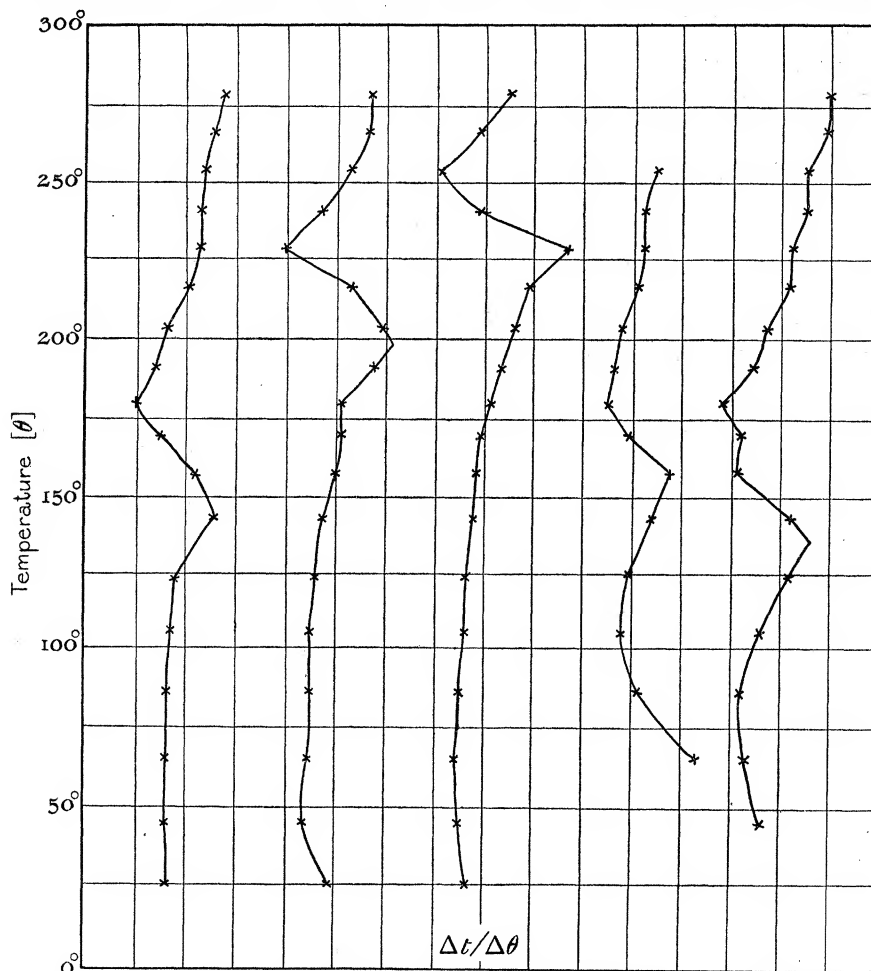


FIG. 6.—Reheating Palladium in Hydrogen.

- No. 1. Active palladium foil after remaining 1 hour in hydrogen at 15° C.
- No. 2. Active palladium foil after remaining 14 hours in hydrogen at 15° C.
- No. 3. Active palladium foil after remaining 8 days in hydrogen at 15° C.
- No. 4. Active palladium button after remaining a short time in hydrogen at 15° C.
- No. 5. Palladium black. The temperature of the critical point being independent of the time of standing in hydrogen.

Note.—A series of curves similar to Nos. 1-3 were also obtained with the palladium button.

palladium foil, exactly similar points are observed as in fig. 4. The palladium button, however, gave no point on first heating in hydrogen, and little evolution

of heat was observed upon admitting the gas. A point on cooling indicated, however, that some gas had been picked up.

A further series of curves in hydrogen was taken, but as the results were in every way similar to those already discussed no further comment is necessary. After this second series of curves the procedure was varied.

It was originally observed by Graham, and confirmed by many other observers, that a portion of the occluded gas could be readily pumped off in the cold, whereas part of the hydrogen is held more tenaciously by the metal, and from the experiments of Holt, Edgar and Firth, it is probable that this easily removed portion represents the adsorbed layer, with no doubt some of the inner dissolved gas. When the metal had completely cooled in hydrogen, the surrounding atmosphere of gas, together with this easily removable portion, was pumped off. Heating curves were then taken, the pump meanwhile removing the rest of the gas as it was evolved. The heating curves are shown in fig. 7 and are of considerable interest.

The curves are of four types. In the case of palladium black, it seemed that all the occluded gas could easily be removed in the cold, and hence the heating curves are not characterised by any points. The gas retained by the metal did not exceed ten volumes.

With palladium foil, two distinct types of curves were obtained, according to whether the metal had remained for a long or a short period of time in hydrogen at room temperature.

When it had only remained a short time, about 120 volumes of gas were evolved on heating, or about 0.1 molecule, and the heating curve showed an evolution of heat which attained a maximum at about 190°C .

When, however, it had remained for a long period in contact with the gas, upwards of 890 volumes of hydrogen were found to have been picked up, which is equal to about 0.75 molecule, and the heating curve showed the familiar point at 190°C , a gradual absorption of heat having taken place from about 130°C . The curve is indeed similar to that shown in fig. 6 for palladium after long standing in hydrogen.

It was remarked that, in the case when about 120 volumes of gas were occluded, the gas on heating was evolved at a rate which the pump could easily cope with. When, however, the volume of gas was greater, it was evolved far too rapidly for the pump to remove, and pressures of 200 to 300 mm. were recorded on the manometer. The failure of the pump to remove the gas as fast as it was evolved resulted in a condition similar to that existing in the experiments shown in fig. 6 where the heating was carried out in an atmosphere of hydrogen.

In the case of the fused button, a condition intermediate between these

two different cases was observed, a result quite borne out by the heating curves.

It has been shown by Hoitsema, that the portions of the pressure-concen-

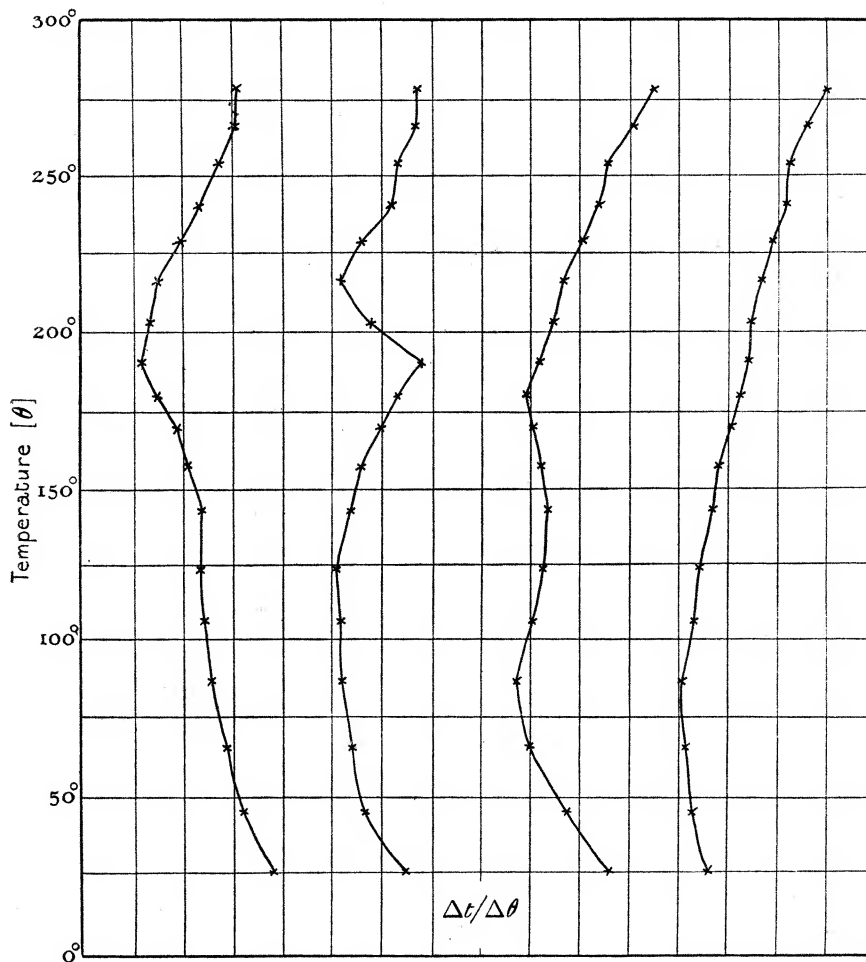


FIG. 7.—Heating Curves of Palladium *in vacuo*.

- No. 1. Palladium foil after remaining a short time in hydrogen at 15° C.
- No. 2. Palladium foil after remaining a long time in hydrogen at 15° C.
- No. 3. Palladium button after remaining a short time in hydrogen at 15° C.
- No. 4. Palladium black. The time of standing in hydrogen not affecting the curve.

tration curves for small concentrations of gas (up to about 0.15 molecule) can be represented by an expression $C/\sqrt{P} = K$, where C is the concentration and P the pressure of the gas, and hence it has been suggested that, at first, the hydrogen is dissolved as atoms. This view is, perhaps, somewhat discounted by the work on absorption of hydrogen by charcoal carried out by

Travers (9), though, on the other hand, it is supported by the work of McBain. It receives distinct confirmation from the heating and cooling curves just described. If the gas was dissolved in atoms, there would be a considerable evolution of heat when it was expelled from the metal, in the ordinary molecular form, and this is precisely what has been observed when only small volumes of gas are pumped out of the metal upon heating. No other simple explanation accounts for an evolution of heat.

Further, above a temperature of about 150°C. , the volume of gas retained by the metal does not greatly vary until the melting point is reached, and this volume of gas (about 0.15 molecule) is very rapidly absorbed. It therefore appears probable that it is this gas which one is dealing with in the above experiments, and which causes the almost constant rise of 7°C. when hydrogen is admitted to palladium in the heated state.

In many of the heating curves of palladium in hydrogen, and also palladium *in vacuo*, after cooling in hydrogen, as in case (vi), it is very noticeable that, after the preliminary absorption of heat indicated in the curve by a movement to the right, the curve, instead of returning to its normal position, moves abruptly towards the left. This deflection in the curve can only be interpreted to mean that the initial absorption of heat is followed by an evolution. This phenomenon is exactly the reverse of what takes place at 15°C. upon admitting hydrogen, when, as it has been remarked, the initial heat evolution is followed by a very rapid cooling. This can be explained on the assumption that, whereas the absorption of heat on heating, and evolution of heat upon admitting hydrogen in the cold, are due to condensation of the gas by the amorphous material, the reverse thermal effects are due to the gas either going into or being driven out of solution of the crystalline mass of the metal.

The evolution of heat is most strongly evident in the curves taken after the metal has been in contact with hydrogen for a considerable time at room temperature, which is entirely what would be expected, the absorption of hydrogen by the crystalline particles having had time to take place.

Although the amorphous phase is meta-stable, and must disappear after being some little time in contact with the crystalline variety, its disappearance at 15°C. is not marked by any evolution of gas, all the gas condensed by the amorphous material being absorbed by the crystalline. The amorphous material merely functions, therefore, as a vehicle conveying hydrogen to the mass of metal. Any possibility of it remaining as a stable phase is contrary to phase-rule considerations.

Discussion of Results and Conclusions.

The thermal behaviour of palladium when heated and cooled *in vacuo* furnishes additional evidence of the dimorphic nature of the metal, the stability of the two forms depending upon the temperature. Owing to the stability of the two modifications when existing separately, and the rate of change from one variety to the other being extremely slow, it seems impossible to bring about any rapid transformation, with the result that only a very slight thermal effect is observed upon heating or cooling through the point of transformation.

A consideration of the results of the heating and cooling curves of palladium in hydrogen, and of the relation they bear to the volume of gas evolved or occluded at varying temperatures, also shows that, whatever the nature of occlusion may be, there is every reason to suppose that the metal exists in two different states, depending upon the temperature and mode of treatment.

In the first place, the metal or its surface layer may be brought into a condition which will enable it to occlude large volumes of hydrogen, with evolution of a considerable quantity of heat, at normal temperatures, the magnitude of the heat evolution and volume of initially occluded gas increasing with the ratio of the surface to the mass of metal.

This rapid occlusion of gas by the metal is most probably due to the presence of an amorphous phase.

This portion of the gas which is occluded rapidly is probably present in the metal in the molecular state, or else exists as molecular complexes, for, upon heating, it is evolved with absorption of heat, the complementary effect to that which took place during occlusion.

The same remark applies to the large volume of gas which is slowly picked up by the metal on standing in hydrogen. It is evolved for the greater part with absorption of heat, the evolution of gas taking place at a higher temperature than is the case when the metal is allowed to remain in contact with hydrogen for short periods of time only.

This alteration in the temperature at which it is evolved is probably the result of the gas having more thoroughly penetrated into the interior of the specimen, necessitating, therefore, greater energy to overcome the passive resistance offered by the metal, and cause it to be driven out.

In the absence of an amorphous film on the surface, palladium may be quite passive with regard to rapid occlusion of gas in the cold; it is highly probable, however, that this passivity is apparent rather than real, and that if sufficient time were allowed for occlusion to take place, a volume of gas equal to that occluded by the active material might eventually go into solution.

At temperatures above 100° C., however, whatever may be the condition of the metal (active or passive) a rapid occlusion of a small quantity of hydrogen invariably takes place with the evolution of constant degree of heat. If, after the occlusion of this small amount of gas, the metal is allowed to cool in hydrogen, no critical points present themselves in the cooling curve. If the metal after being allowed to cool in this manner is now heated *in vacuo*, a small evolution of heat is found to occur.

The most feasible explanation of the above phenomena is that, following the initial occlusion of gas molecules, which gives rise to a small evolution of heat, there occurs a splitting up of the molecules into atoms. When this gas is expelled, therefore, an evolution of heat will be indicated, owing to the combination of atoms to form molecules. The cause of the complementary effect not being realised upon admitting the gas to the metal at this temperature is undoubtedly the initial heat evolution, due to adsorption of the gas in the molecular form, and also the fact that the breaking up of the molecules into atoms is not sufficiently spontaneous to give any observable effect.

Hydrogen may be dissolved by both the crystalline and amorphous varieties of the metal, but whilst in presence of the amorphous phase solution of hydrogen is extremely rapid, when this phase is not present solution takes place but slowly. The amorphous phase appears to function as a vehicle for the transference of hydrogen to the crystalline phase.

That temperature is an important factor is quite evident, when it is considered that above a certain temperature all varieties of palladium cease to occlude hydrogen in any quantity. In fact, it may be stated that above 150° C. all forms of the metal have an equal affinity for the gas.

In conclusion the authors wish to express their indebtedness to Prof. Carpenter for the kind interest he has taken, and for the facilities which have enabled them to carry out their investigation.

BIBLIOGRAPHY.

1. Hoitsema, 'Zeit. f. Physik. Chemie,' 1895, vol. 17, p. 1.
 2. Sieverts, 'Zeit. f. Electrochemie,' vol. 16, p. 709; 'Ber.,' vol. 43, p. 897; 'Internat. Zeit. f. Metallographie,' vol. 3, p. 51 (Table XII).
 3. Ramsay, Mond, and Shields, 'Roy. Soc. Proc.,' 1897, vol. 62, p. 290; 'Phil. Trans.,' 1898, A, vol. 191, p. 105.
 4. Holt, Edgar, and Firth, 'Zeit. f. Physik. Chemie,' 1913, vol. 82, p. 5.
 5. Andrew, 'Journ. Iron and Steel Inst.,' 1911 (Carnegie Memoirs), No. 3.
 6. Beilby, 'Journ. Inst. of Metals,' 1911, No. 2.
 7. Bengough, 'Journ. Inst. of Metals,' 1912, No. 1.
 8. Rosenhain and Ewen, 'Journ. Inst. of Metals,' 1912, No. 2.
 9. Travers, 'Roy. Soc. Proc.,' A, 1906, vol. 78, p. 9.
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